

PATENT ABSTRACTS OF JAPAN

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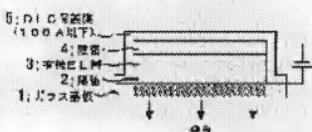
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(54) DLC PROTECTIVE FILM, ORGANIC EL ELEMENT USING THE SAME AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an organic EL element having sufficient adhesion and fineness of a film and a protective film with a thin film thickness formed in it.

SOLUTION: In this organic EL element, an anode 2, an organic EL element layer 3 and a cathode 4 are laminated in this order on a glass substrate 1, and a DLC protective film 5 is formed on the glass board so as to cover them. The DLC protective film is structured by laminating a backing film 6 of amorphous silicon and at least two or more layers of DLC, and among the laminated layers, a first protective carbon film 7 adhering to the backing film formed on the glass board is formed by a CVD method or a spattering method under the condition having a partial hydrogen pressure of about 20% in which internal stress gets small, and a second carbon film 8 laminated on its top is formed by the CVD method or the spattering method under the condition in which hydrogen growing its density is not practically contained.



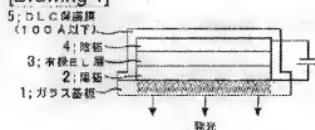
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DRAWINGS

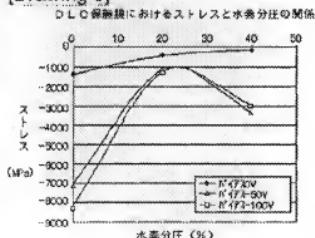
[Drawing 1]



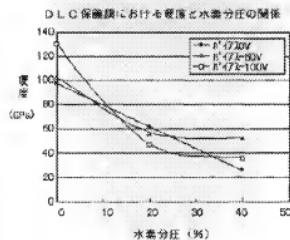
[Drawing 2]



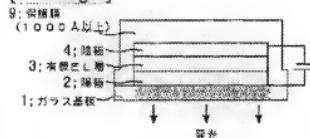
[Drawing 3]



[Drawing 4]



[Drawing 5]



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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view for explaining the structure of the organic EL device concerning one example of this invention.

[Drawing 2]It is a sectional view for explaining the structure of the DLC protective film concerning one example of this invention.

[Drawing 3]It is a figure for explaining the relation between the DLC protective film stress concerning one example of this invention, and hydrogen content pressure.

[Drawing 4]It is a figure for explaining the relation between the DLC protective film hardness concerning one example of this invention, and hydrogen content pressure.

[Drawing 5]It is a sectional view for explaining the conventional organic EL device.

[Description of Notations]

- 1 Glass substrate
- 2 Anode
- 3 Organic electroluminescence layer
- 4 Negative pole
- 5 DLC protective film
- 6 Amorphous Si film
- 7 The 1st carbon protective film
- 8 The 2nd carbon protective film
- 9 Protective film

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to an organic EL device which has the protective film formed with hydrogenation carbon, and a manufacturing method for the same about an organic electroluminescence (electro-luminescence) element and a manufacturing method for the same.

[0002]

[Description of the Prior Art] In order to realize the rise in luminosity of an organic EL device conventionally, a material excellent in electron injections, such as alkaline metals, is used as a cathode material, but on the other hand there is a problem that reactivity is high, between oxygen, moisture, etc. Although material with high luminous efficiency is similarly used in organic electroluminescence material, chemicals degradation arises with oxygen and the moisture in the atmosphere, and there is a possibility that luminescent characteristics, such as luminosity and a chromaticity, may fall.

[0003] Here, it explains, referring to drawings for the conventional organic EL device. Drawing 5 is a sectional view of the conventional organic EL device. As shown in drawing 5, the conventional organic EL device is constituted by forming the anode (transparent electrode) 2 which consists of ITO(s) (indium tin oxidation thing) on the glass substrate 1, and forming the organic electroluminescence layer 3 and negative pole 4 grades, such as a hole-injection transporting bed, a luminous layer, and an electron injection transporting bed, on this. The protective film 9 is made to cover here for the corrosion prevention of a cathode part and an organic electroluminescence layer.

[0004] Although protective films, such as SiO_2 and Si_3N_4 , are made to cover with JP,8-111286,A about this protective film, in order to make the life of an element hold for a long period of time, not less than 100 nm of protective film thickness is needed. In JP,5-101885,A, the diamond Mr. thin film by the ionization vacuum deposition which has Vickers hardness more than 2 of 3000-8000kg/mm is made to form in the organic electroluminescence layer surface, and the thickness at this time is 0.5 micrometers or more. In JP,63-259994,A, the EL element is made to seal with the amorphous-like carbon film which consists of a carbon atom and a hydrogen atom, and the thickness at this time supposes that several 10 nm - about several micrometers are suitable.

[0005]

[Problem(s) to be Solved by the Invention] Thus, also in which conventional example mentioned above, although carbon, such as SiO_2 and Si_3N_4 , is used as a protective film of an organic EL device, The composition which laminates continuously the carbon film more than the bilayer from which membrane characteristics differ in these protective films is not described. Also in the conventional example which is making the carbon film cover, there is nothing on which high adhesion and high hardness (high-density) peculiar to a carbon film are made to act effectively. Therefore, total thickness also including the ground film thickness of these protective films needs not less than several 10 nm.

[0006] Protective films of step coverage, such as the conventional SiO_2 and Si_3N_4 , are [the reason] insufficient, and it is not precise. Even if it makes a carbon film cover, as long as this is monolayer, if film adhesion is thought as important, the optimal film hardness will not be obtained, and if film hardness is thought as important on the contrary, the optimal film adhesion will not be acquired. Therefore, it is because film adhesion and the protective film with which it is satisfied of the both sides of film hardness are not obtained as long as it is monolayer.

[0007] It is in providing an organic EL device with which this invention was made in view of the above-mentioned problem, and the main purpose had the adhesion and compactness of sufficient film, and the thin protective film of thickness was formed, and a manufacturing method for the same.

[0008]

[Means for Solving the Problem] To achieve the above objects, in the 1st viewpoint, this invention on a substrate, They are a ground film and a protective film which laminates DLC (diamond like carbon) more than two-layer at least, A DLC layer stuck to said ground film formed in said substrate is formed by hydrogen content pressing down predetermined [that internal stress becomes small], At least one layer other than said DLC layer stuck to said ground film among said protective films is formed under conditions which do not contain substantially hydrogen that density becomes large.

[0009] This invention is a manufacturing method of a protective film which laminates DLC more than two-layer on a substrate at least with a ground film in the 2nd viewpoint, (a) A process of forming the 1st DLC layer stuck to said ground film formed in said substrate under conditions of 20% of hydrogen content pressure abbreviation which becomes small [internal stress], (b) Include at least a process of forming hydrogen which becomes large [density] about the 2nd DLC layer under conditions which are not included substantially on said 1st DLC layer.

[0010] In an organic EL device with which a protective film is formed on said glass substrate so that the anode, an organic electroluminescence layer, and the negative pole may be laminated by this order on a glass substrate and this invention may cover these in the 3rd viewpoint, Said protective film makes a ground film which consists of amorphous silicon, and structure which laminated DLC more than two-layer at least, A layer stuck to said ground film formed in said glass substrate among protective films of said laminated structure is constituted by the 1st DLC layer with small internal stress, and at least one layer other than said 1st DLC layer is constituted by the 2nd DLC layer with large density.

[0011] In this invention, it is preferred that thickness of said protective film is 10 nm or less, and it can also have composition of said protective film in which the above is further formed with hydrogenation

carbon at least.

[0012]In this invention, it is preferred that it is the film in which said 1st DLC layer was formed under conditions of 20% of hydrogen content pressure abbreviation, said 2nd DLC layer was formed under conditions which do not contain hydrogen substantially, and said 1st DLC layer or the 2nd DLC layer was formed of a CVD method or a sputtering technique.

[0013]This invention on a glass substrate in which (a) anode, an organic electroluminescence layer, and the negative pole were laminated by this order in the 4th viewpoint, A process of forming the 1st DLC layer after ground film formation which consists of amorphous silicons under conditions of 20% of hydrogen content pressure abbreviation that stress becomes small, (b) Include at least a process of forming hydrogen that density becomes large about the 2nd DLC layer, under conditions which are not included substantially on said 1st DLC layer.

[0014]

[Embodiment of the Invention]In the desirable 1 embodiment the organic EL device concerning this invention, The anode (2 of drawing 1), an organic electroluminescence layer (3 of drawing 1), and the negative pole (4 of drawing 1) are laminated by this order on a glass substrate (1 of drawing 1), It is the organic EL device with which the DLC protective film (5 of drawing 1) is formed on the glass substrate so that these may be covered, A DLC protective film makes the ground film (6 of drawing 2) which consists of amorphous silicons, and the structure which laminated DLC more than two-layer at least, The 1st carbon protective film (7 of drawing 2) sticking to the ground film formed in the glass substrate among the lamination is formed by a CVD method or the sputtering technique under the conditions which are 20% of hydrogen content pressure abbreviation to which internal stress becomes small, The 2nd carbon protective film (8 of drawing 2) laminated on it is formed by the CVD method or the sputtering technique under the conditions which do not contain substantially hydrogen that density becomes large.

[0015]Adhesion with the negative pole or a glass substrate can be protected by a layer with internal stress small for making the protective film of an organic EL device into such a structure, and an organic EL device can be protected from oxygen or moisture by a layer with compactness high with slight height. Total thickness can be used as a thin film of 10 nm or less by optimizing the film formation condition of each class.

[0016]

[Example]The above-mentioned embodiment of the invention is described below with reference to drawing 1 thru/or drawing 4 about the example of this invention that it should explain still in detail. Drawing 1 is a sectional view for explaining typically the structure of the organic EL device concerning one example of this invention.

Drawing 2 is a sectional view showing the structure of a DLC protective film.

Drawing 3 is a figure showing the stress of a DLC protective film, and the relation of hydrogen content pressure.

Drawing 4 is a figure showing the hardness of a DLC protective film, and the relation of hydrogen content pressure.

[0017]As shown in drawing 1, the organic EL device of this example, It is constituted by forming the anode (transparent electrode) 2 which consists of ITO(s) (indium tin oxidation thing) on the glass substrate 1 like a conventional example, and forming the organic electroluminescence layer 3 and negative pole 4 grades, such as a hole-injection transporting bed, a luminous layer, and an electron injection transporting bed, on this. The DLC protective film 5 is made to cover with this example for the corrosion prevention of a cathode part and an organic electroluminescence layer.

[0018]As shown in drawing 2, this DLC protective film 5 is an insulator layer constituted by DLC, and is formed by a CVD method or the sputtering technique at low temperature. A method for film deposition forms amorphous Si film 6 as a ground film to the negative pole 4 first. At this time, before forming an amorphous Si film, reverse sputtering may be given as pretreatment, and the negative pole 4 surface may be defecated.

[0019]Next, although the 1st carbon protective film 7 is formed, it is the feature that this 1st carbon protective film 7 forms membranes under the conditions from which hydrogen content pressure will be abbreviated 20% (20 to 25%). The reason is because stress of the DLC protective film 5 can be made the smallest, when membranes are formed under the conditions whose hydrogen content pressure is abbreviated 20%, as shown in drawing 3 showing the hydrogen content pressure at the time of DLC membrane formation, and the relation of stress (internal stress). That is, it is because exfoliation of the DLC protective film 5 can be controlled and adhesion with the glass substrate 1 or the negative pole 4 can be improved, if membranous stress is small.

[0020]The 2nd carbon protective film 8 is formed and the carbon protective film of a bilayer is made to form on it. It is the feature that this 2nd carbon protective film 8 forms hydrogen under the conditions (for example, hydrogen content pressure 0%) which are not included substantially. This is because the direction which hydrogen content pressure formed on few conditions can make the highest hardness (film density) of the DLC protective film 5, as shown in drawing 4 showing the relation of the hydrogen content pressure and hardness (film density) at the time of DLC membrane formation. That is, it is because it will become can control that oxygen and moisture permeate a film and possible to make thickness required as a protective film thin if the density of a film is high.

[0021]here -- an amorphous Si film -- about 1-2 nm, and the 1st carbon protective film 7 and 2nd carbon protective film 8 -- about 3 in all-8 nm -- with -- it is good, therefore is 10 nm or less as total as thickness of a DLC protective film.

Compared with the former, it comprises a super-thin film.

[0022]Thus, in the composition of this example, stress raises adhesion with the negative pole with the 1st small good carbon protective film of step coverage, It can control that oxygen and the moisture in the atmosphere penetrate to a cathode part and an organic electroluminescence layer with the 2nd carbon protective film with high hardness (film density) as much as possible. Therefore, though it is thin thickness compared with the former, it can fully function as a protective film.

[0023]In this example, although the example of two-layer structure was explained as a structure of a DLC protective film, this invention is not limited to the above-mentioned example, and even if it laminates the hydrogenation carbon protective film of three or more layers, for example, it does the

same effect so. This carbon protective film is formed by a CVD method or the sputtering technique at low temperature.

[0024]

[Effect of the Invention]As explained above, according to this invention, also in a high-humidity/temperature environment, the corrosion of the cathode part by oxygen and the moisture in the atmosphere and an organic electroluminescence layer can be controlled, therefore the life characteristic of an organic EL device improves, and the effect that long-term reliability can be acquired is done so.

[0025]Since the reason is constituted by the 1st carbon protective film with small stress and a DLC protective film of this invention good [step coverage], and the 2nd carbon protective film with a precise film, It is because it excels in adhesion with a substrate and a cathode part and an organic electroluminescence layer can be protected from oxygen and the moisture in the atmosphere.

[0026]According to the composition of this invention, since a DLC protective film can be made to cover with a super-thin film of 10 nm or less, it also has the effect that a thin organic electroluminescence display can be provided.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]It is a protective film which laminates DLC (diamond like carbon) more than two-layer at least with a ground film on a substrate, A DLC layer stuck to said ground film formed in said substrate is formed by hydrogen content pressing down predetermined [that internal stress becomes small], A protective film characterized by what is formed under conditions in which at least one layer except said DLC layer stuck to said ground film among said protective films does not contain substantially hydrogen that density becomes large.

[Claim 2]The protective film according to claim 1 characterized by what said predetermined hydrogen content pressure is abbreviated 20%.

[Claim 3]A process of forming the 1st DLC layer stuck to said ground film which is a manufacturing method of a ground film and a protective film which laminates DLC more than two-layer on a substrate at least, and was formed in the (a) aforementioned board under conditions of 20% of hydrogen content pressure abbreviation which becomes small [internal stress], (b) A manufacturing method of a protective film including at least a process of forming hydrogen which becomes large [density] about the 2nd DLC layer under conditions which are not included substantially on said 1st DLC layer.

[Claim 4]In an organic EL device with which a protective film is formed on said glass substrate so that the anode, an organic electroluminescence (electro-luminescence) layer, and the negative pole may be laminated by this order on a glass substrate and these may be covered, An organic EL device characterized by what said protective film laminates DLC more than two-layer at least with a ground film which consists of amorphous silicons, and is constituted for.

[Claim 5]In an organic EL device with which a protective film is formed on said glass substrate so that the anode, an organic electroluminescence layer, and the negative pole may be laminated by this order on a glass substrate and these may be covered, Said protective film makes a ground film which consists of amorphous silicons, and structure which laminated DLC more than two-layer at least, An organic EL device characterized by what a layer stuck to said ground film formed in said glass substrate among protective films of said laminated structure is constituted by the 1st DLC layer with small internal stress, and at least one layer other than said 1st DLC layer is constituted for by the 2nd DLC layer with large density.

[Claim 6]The organic EL device according to claim 4 or 5 characterized by what thickness of said protective film is 10 nm or less.

[Claim 7]The organic EL device according to claim 4 to 6 characterized by a thing of said protective film for which the above is further formed with hydrogenation carbon at least.

[Claim 8]The organic EL device according to any one of claims 4 to 7 with which said 1st DLC layer is characterized by what is formed under conditions of 20% of hydrogen content pressure abbreviation.

[Claim 9]The organic EL device according to any one of claims 4 to 8 characterized by what said 2nd DLC layer is formed for under conditions which do not contain hydrogen substantially.

[Claim 10]The organic EL device according to any one of claims 4 to 9 characterized by what said 1st DLC layer or the 2nd DLC layer is the film formed by a CVD method.

[Claim 11]The organic EL device according to any one of claims 4 to 9 characterized by what said 1st DLC layer or the 2nd DLC layer is the film formed of a sputtering technique.

[Claim 12](a) A process of forming the 1st DLC layer under conditions which are 20% of hydrogen content pressure abbreviation to which internal stress becomes small after ground film formation which consists of amorphous silicons on a glass substrate in which the anode, an organic electroluminescence layer, and the negative pole were laminated by this order, (b) A manufacturing method of an organic EL device characterized by what a process of forming hydrogen that density becomes large about the 2nd DLC layer, under conditions which are not included substantially on said 1st DLC layer is included for at least.

[Claim 13]A manufacturing method of the organic EL device according to claim 12 characterized by what said 1st DLC layer or said 2nd DLC layer is formed for with a CVD method.

[Claim 14]A manufacturing method of the organic EL device according to claim 12 characterized by what said 1st DLC layer or said 2nd DLC layer is formed for by a sputtering technique.

[Claim 15]An organic electroluminescence display which carries the organic EL device according to any one of claims 4 to 11.

[Translation done.]